

PCT/GB 00 / 02301



INVESTOR IN PEOPLE

09/763641

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

JKU

REC'D 16 AUG 2000

WIPO

PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Ambraser

Dated

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

THIS PAGE BLANK (USPTO)

14 JAN 2000

Request for grant of a patent

See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form.

The Patent Office

Cardiff Road

Newport

Gwent NP9 1RH

Your reference

BKCD/NS/DBN.105(a)

14 JAN 2000

Patent application number

(The Patent Office will fill in this part)

0000780.7

Full name, address and postcode of the or of each applicant (underline all surnames)

Trikon Holdings Limited
Coed Rhedyn
Ringland Way
Newport, Gwent
NP6 2TA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

Title of the invention

A Method of Processing a Polymer Layer

Name of your agent (if you have one)

Wynne-Jones, Laine & James

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

22 Rodney Road
Cheltenham
GL50 1JJ

Patents ADP number (if you know it)

1792001

If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Yes

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description	6 ✓
Claim(s)	0
Abstract	0 SV
Drawing(s)	6 7

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

1. I/We request the grant of a patent on the basis of this application.

Signature	Date
Wynne-Jones, Laine & James	14.01.2000

2. Name and daytime telephone number of person to contact in the United Kingdom	Mr. B. Dunlop	01242 515807
---	---------------	--------------

Warning
After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes
If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
Write your answers in capital letters using black ink or you may type them.
If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
If you have answered 'Yes' Patents Form 7/77 will need to be filed.
Once you have filled in the form you must remember to sign and date it.

A Method of Processing a Polymer Layer

In our pending British Patent Application 9922801.7, which is incorporated herein by reference we discuss the use of a plasma treatment during the step of heating a polymer layer to desorb moisture and harden the layer and exposing the layer to a plasma during that heating process. In the preliminary discussion, it was perceived that the main benefit of this procedure was to reduce cracking in the polymer layer, but it was noted that the plasma treatment was significantly changing the film structure as shown by the FTIR.

It has now been established that further surprising benefits can be obtained if low k films are treated in this manner and these will be described in connection with the following drawings in which:

Figure 7 and 8 plot dielectric constant against plasma heating time at various temperatures and generally correspond with Figure 4;

Figures 9 to 12 illustrate the effect of strip process on k-value; and Figure 13 indicates k value stability.

It will be again seen from Figures 7 and 8, that combination of heat and plasma exposure time affect the k-value achieved for example a 3 minute plasma exposure at

350°C or a 2 minute exposure at 400°C appear particularly efficacious.

Looking at the benefits of the treated films the wet etch rate of hydrogen treated films using a 10:1 BOE (buffered oxide etch) at 20°C are typically similar to or less than that of thermal oxide i.e. around 550 Å/min. The untreated films etch at over 10,000 Å/min. Accordingly the hydrogen plasma treatment therefore reduces the wet etch rate by a factor of 20 or more. Wet etch rate is generally used as an indication of merit for silicon dioxide layers where thermal oxide is considered to be of high quality.

It has been determined that hydrogen plasma treatment is effective to varying depths dependent on the time of the process and the composition of the film. In general the lower the k value the greater the depth of treatment. Thus for a k=2.7 film, the treatment penetrated to a depth of 3,000 Å whilst with a K-2.4 film the depth of treatment was 5,700 Å. Both tests were carried out under the following conditions:

Hydrogen Flow	1000 sccm
Platen Temperature	400°C
RF Power	1000 Watts
RF Frequency	13.56 MHz
Pressure	4 Torr
Electrode Spacing	6mm
Time	300 seconds

It has been found that increasing the power level or changing the electrode spacing does not significantly increase the effective depth of the plasma treatment, but increasing the treatment time to 600 seconds increases the depth of treatment on the $K=2.7$ film from 3000 Å to 6000 Å. (i.e. twice the time, twice the depth).

It will have been noted from our earlier application that the hydrogen treatment also improves, i.e. lowers, the k value. It was considered desirable to determine whether this k value improvement could be achieved for the bulk of the material, even if only a surface treatment took place. Accordingly a 6000 Å, $k=2.7$ film was formed first by depositing two 3000 Å layers, each of which were treated with a hydrogen plasma for 300 seconds. Secondly 6000 Å layers were deposited and treated for either 300 or 600 seconds. No variation in k value was determined. This appears to show that the film that was only treated to half its depth is still yielding an improved k value of the previous best known method of a vacuum thermal process, which is presumed to give a bulk effect. It is thus postulated that the hydrogen plasma is effective at reducing k values even as a surface treatment perhaps by reducing the likelihood of water re-absorption whilst the

applied heat may be a bulk effect performing the bulk moisture disorption from the as-deposited layer. They hydrogen plasma clearly changes the bonding composition as evidenced by the FTIR data yielding an as-treated layer that etches slower and providing a treated layer that protects the underlying part of the layer from subsequent plasma etch processes and presumably water re-absorption. Thus the hydrogen plasma is effective on a heated layer at improving at least a surface of that layer to the benefit of the whole layer, the improvement being an improvement in the layers usefulness as a low k dielectric in a semiconductor device.

It had previously been found that if the low k films were subjected to oxygen based resist stripping process necessary if low k films are to be integrated into subtractive and damascene schemes using standard processes then carbon tended to be stripped out of the films and presumably replaced by water accompanied by a substantial increase in the k value.

Although Figures 5 and 6 of British Application 9922801.7 indicate that the C-H and SiH bonds are reduced by the hydrogen plasma, resultant structure appears to be stable under strip process.

Thus turning to Figures 9 to 12 the integrated peak area ratios for the various indicated bonds are not changed substantially by an oxygen based stripping process. Similarly the effects of the oxygen and hydrogen (reducing) resist strips are shown on the hydrogen plasma treated films reactive indexes in Figures 11 and 12. Refractive index is an indirect indication of k value.

The hydrogen plasma treatment is thus shown to provide an effective barrier to a subsequent oxygen-based plasma process.

In order to ascertain the stability of the k value wafers were blanket coated in a $k=2.7$ Si-C polymer and were then subjected to a standard fluorine based dielectric etch process, followed by a hydrogen plasma (reducing) resist strip process to simulate conditions on the exposed parts of a patterned etched dielectric structure. The dielectric constant was shown (see Figure 13) to remain at 2.7 after these etch and strip processes and to be stable over time. After 48 hours the k value had increased slightly. A 450°C anneal brought the k value back down to 2.7 and after a further 48 hours the k value had increased only very slightly.

The improvement in the surface layer of the low k dielectrics such that its wet etch rate equates to that of

a thermal oxide may be particularly advantageous in connection with chemical mechanical polishing. The mechanical/chemical abrasion of low k dielectrics of the nano-porous and/or carbon containing kind presents a problem as they are typically of low density and have poor mechanical strength. Attempts to chemical mechanical polish such layers tends to cause dishing of the dielectric between the areas of metalisation. This should be less apparent with low k films which have been treated according to the invention.

The advantage of using a hydrogen plasma on a heated wafer were also recognised in our co-pending application No. 99044273. This in particular indicates that hydrogen mixed with etch gas may maintain or enhance the low k structure during etching. It would therefore be particularly advantageous to use that approach when etching materials prepared in accordance with 9922801.7 or this application.

It has also been appreciated that if the surface of the low k material is treated as described in 9922801.7 or this application then it will be possible in at least certain cases to dispense with the capping layer that has been used to date and thus compensate for the rather long cycle times which were mentioned in 9904427.3.

Dielectric Constant vs Hydrogen Plasma Treatment Time

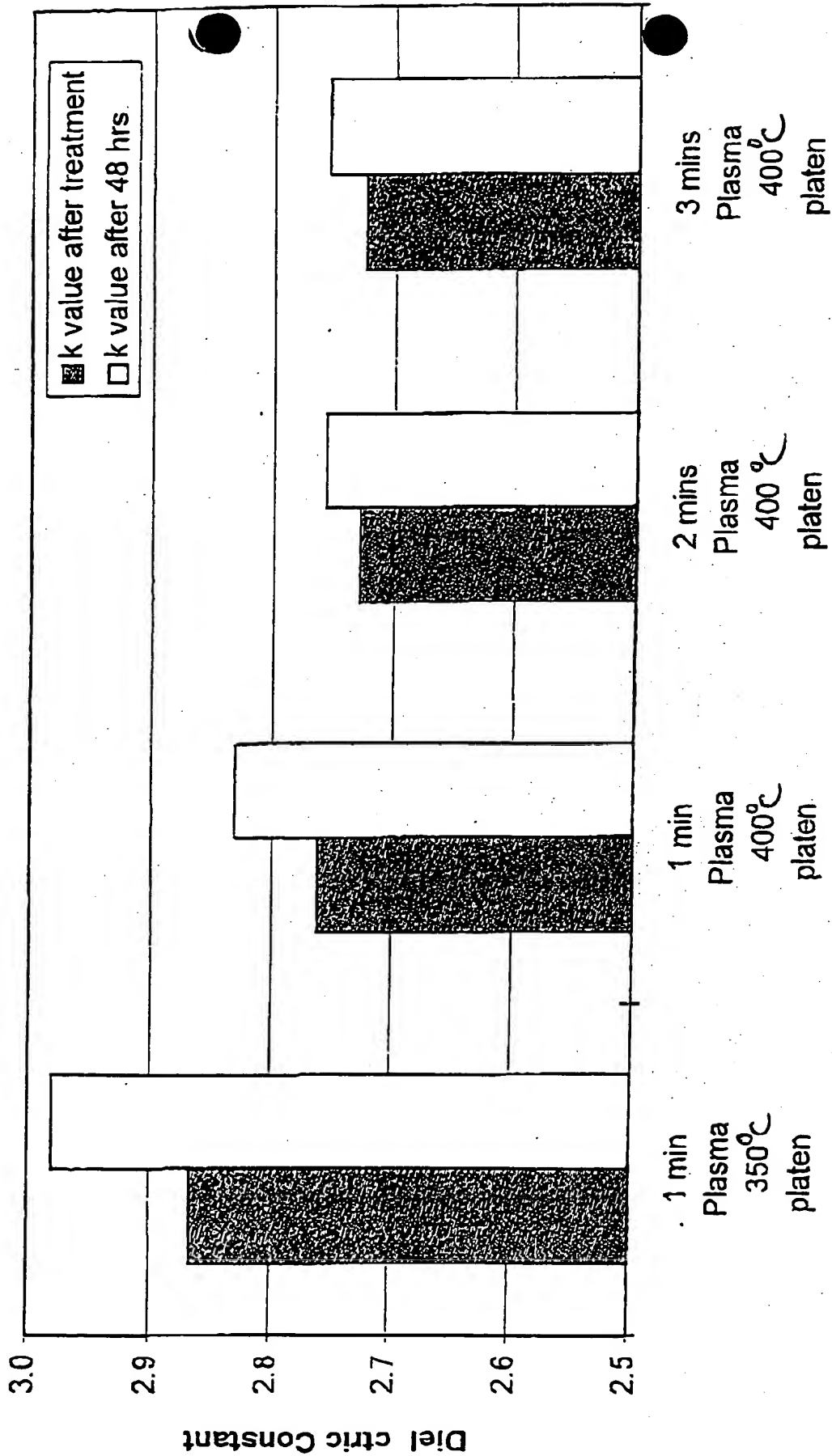


FIG 7

THIS PAGE BLANK (USPTO)

Dielectric Constant vs Hydrogen Plasma Treatment Temperature

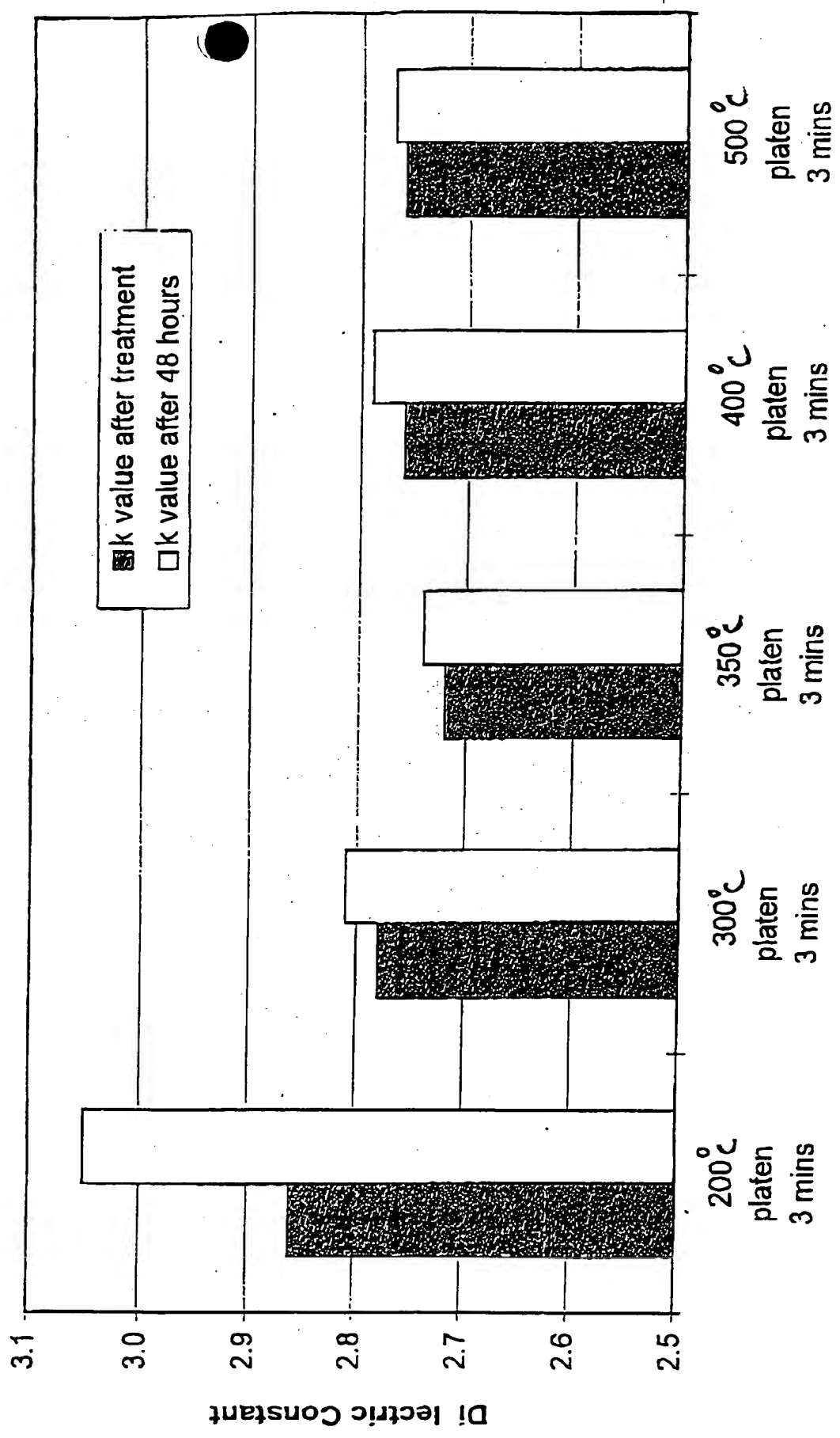
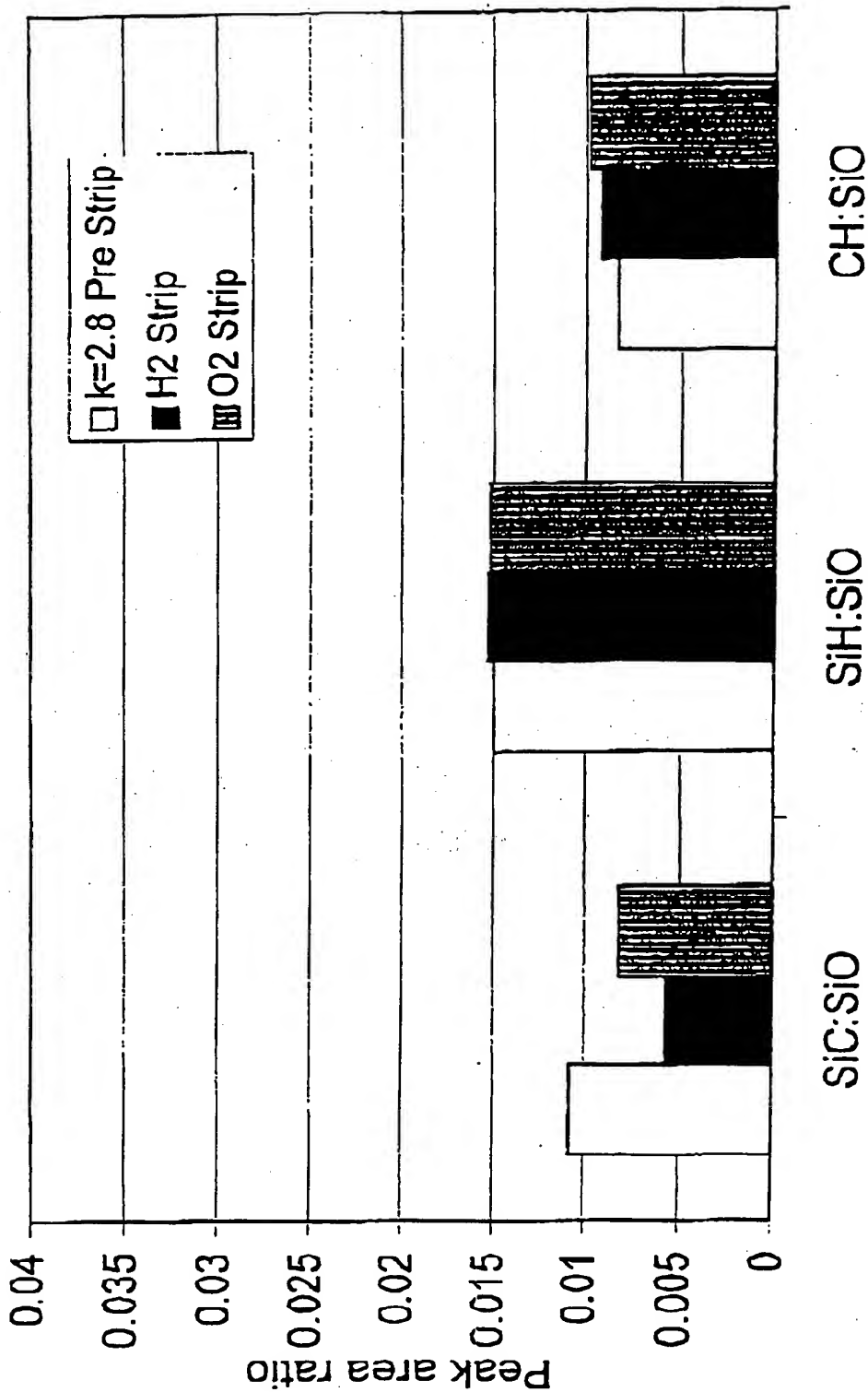


FIG-8

THIS PAGE BLANK (USPTO)

Effect of hydrogen and oxygen strip on Flowfill (k=2.8) treated with H2 plasma

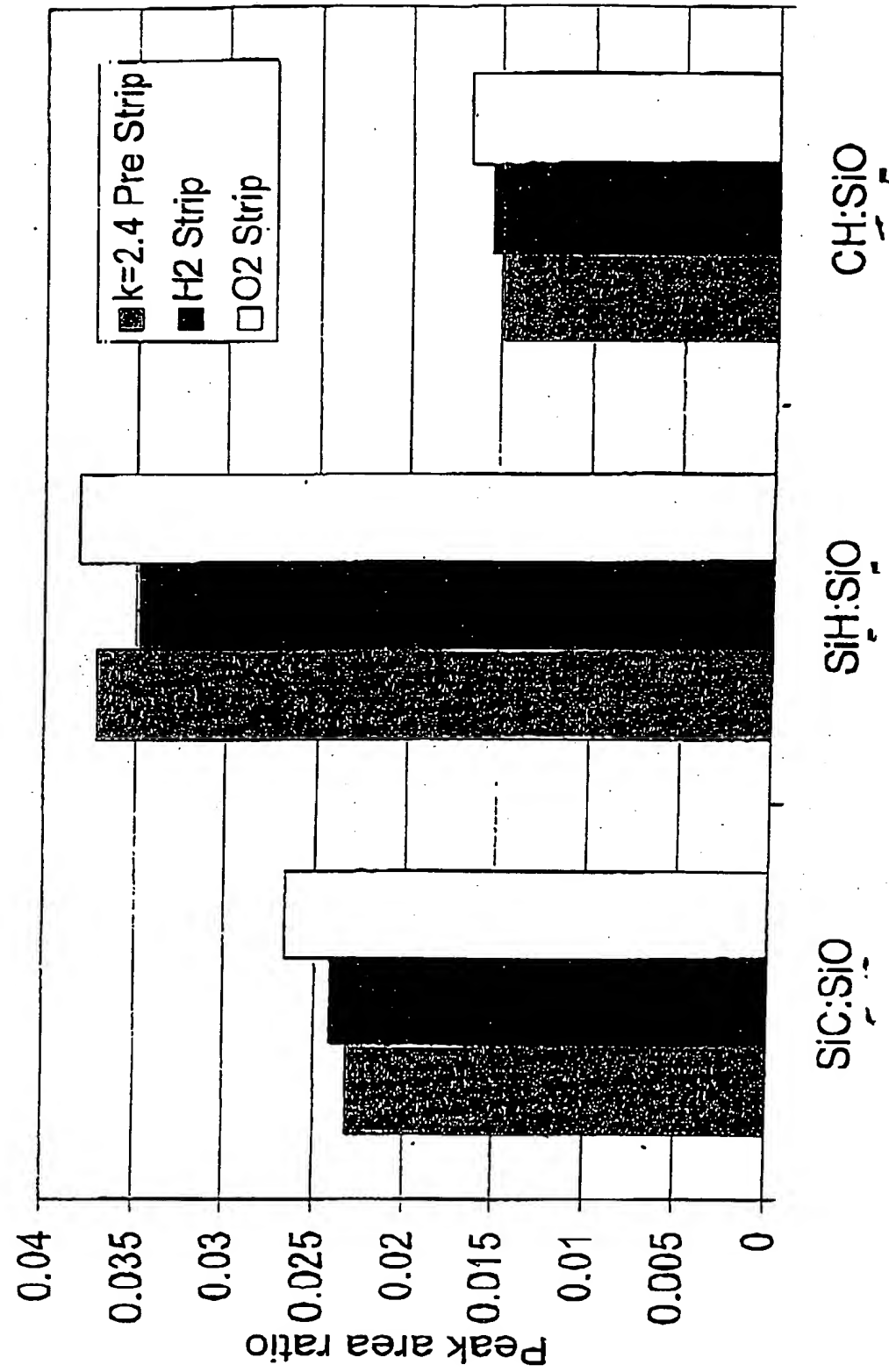


Integrated peak area ratios
FIG 9

THIS PAGE BLANK (USPTO)

Effect of hydrogen and oxygen strip on Flowfill (k=2.4) treated with H2

plasma



Integrated peak area ratios
FIG 10

THIS PAGE BLANK (USPTO)

Effect of hydrogen and oxygen strip on Flowfill (k=2.8) treated with H2 plasma

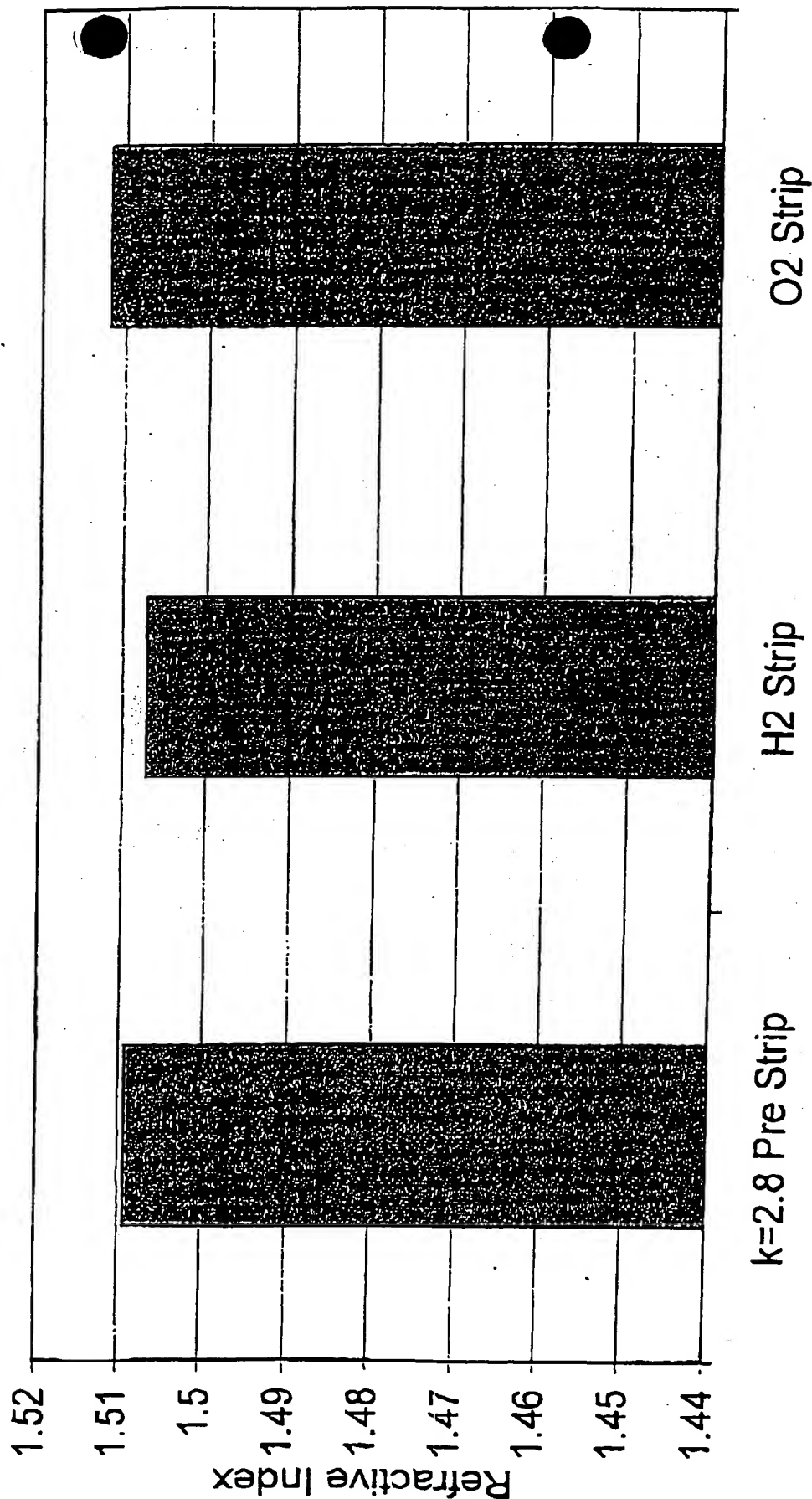


FIG 11

)

THIS PAGE BLANK (USPTO)

A vertical black line is located in the bottom right corner of the page.

Effect of hydrogen and oxygen strip on Flowfill (k=2.4) treated with H2 plasma

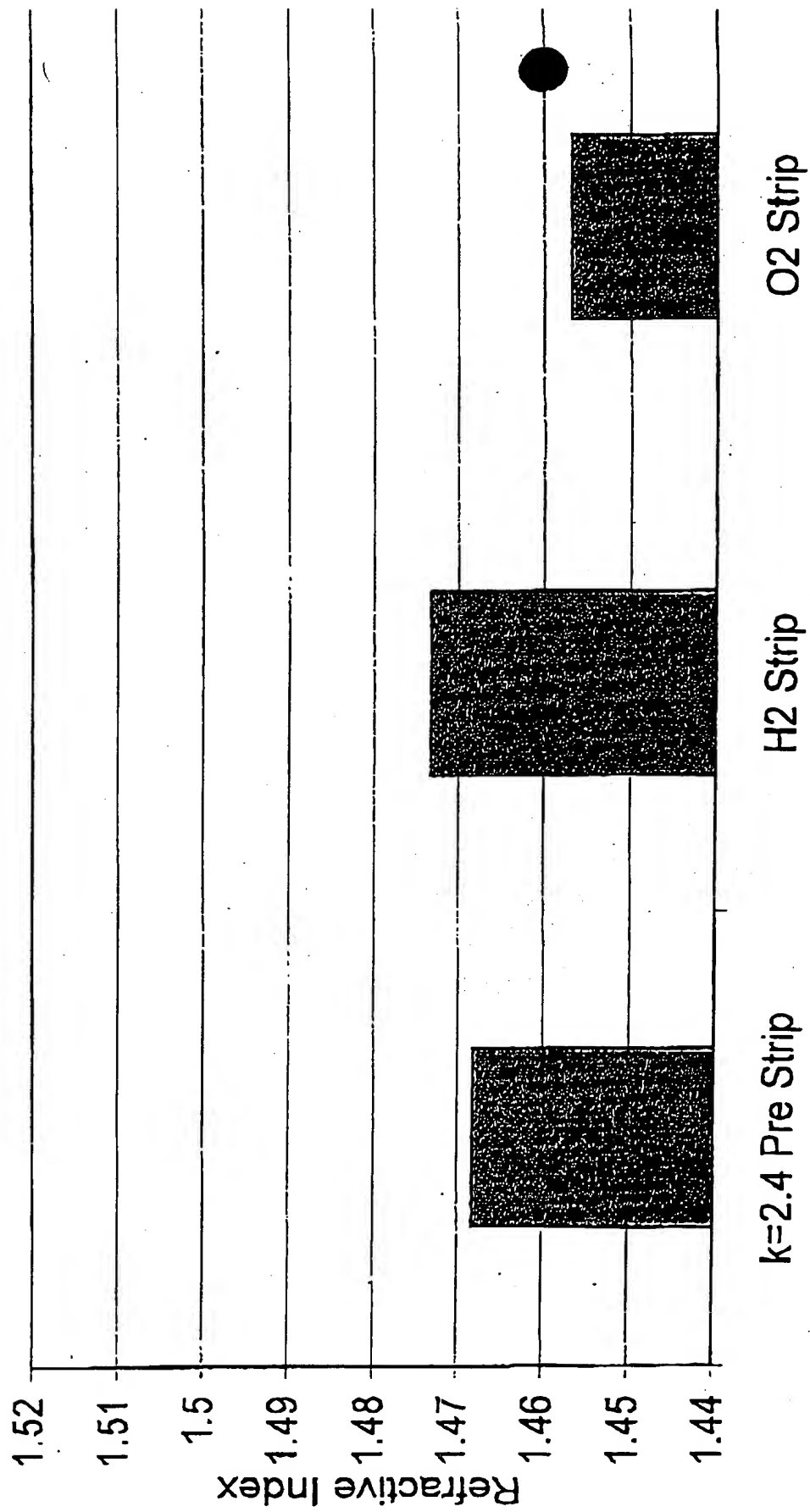


FIG 12

)

THIS PAGE BLANK (USPTO)

A vertical black line is located in the bottom right corner of the page.

Dielectric Constant Stability Post Reducing Strip Process 90 Second Strip on Blanket Film with No Resist

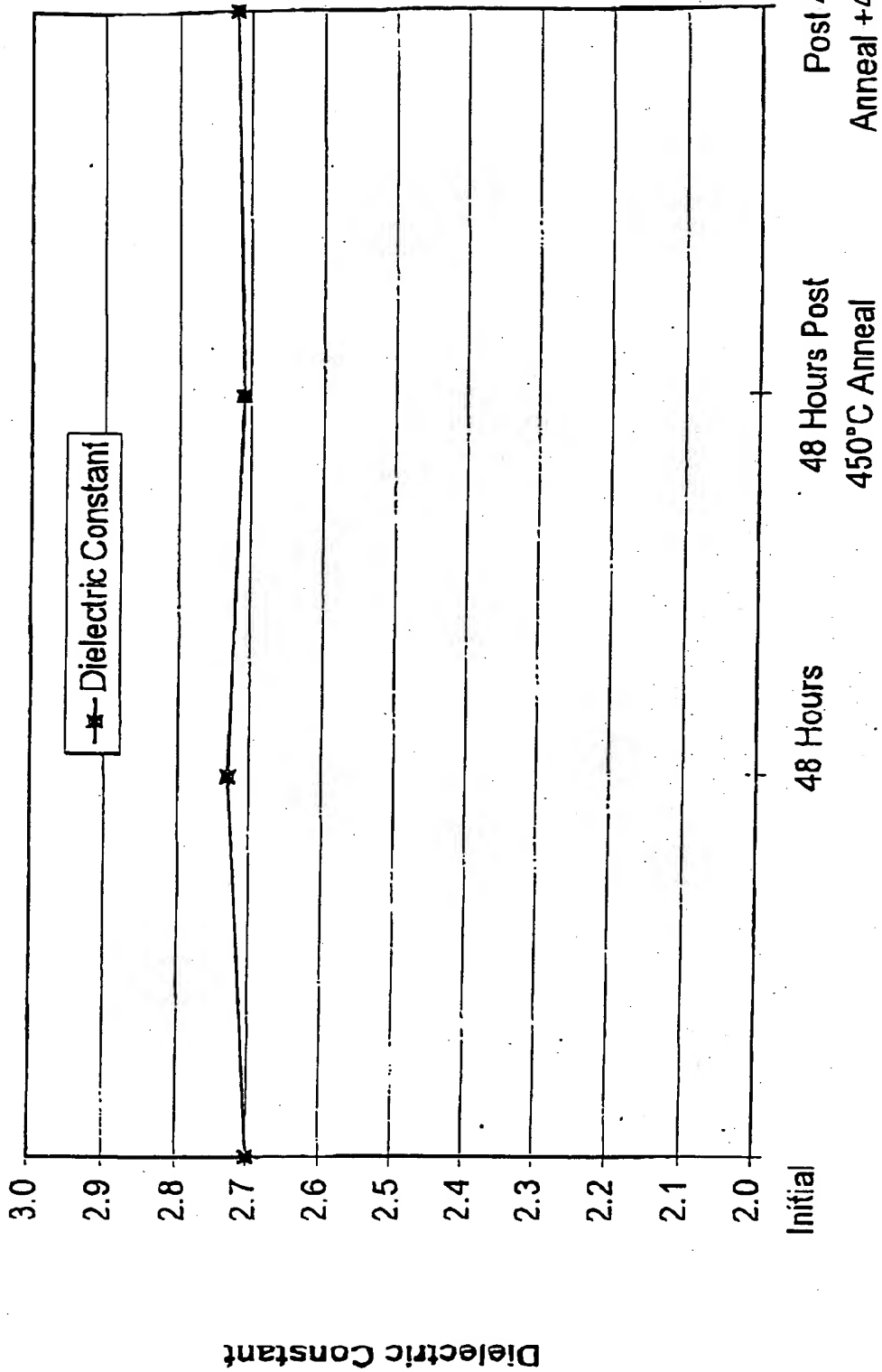


FIG 13.

P752 31/3/98

PCT 19B00/023

6.7.00

Wynne-Jones Laine & James